Computer Simulations and Crossover Equation of State of Square-Well Fluids with Variable Width.

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The square-well systems capture the essential features of real materials while remaining simple enough to treat using analytic and simulation methods. Because of its simplicity, the square-well fluid (SWF) has long served as a model system for understanding the behavior of real fluids. In the present work, we perform extensive new molecular dynamics (MD) and Monte Carlo (MC) simulations in the one-phase region for the SWF with well widths of λ = 1.25, 1.375, 1.5, 1.75, 1.90, 2.0, 2.1, and 3.0. These data together with MD and MC data reported earlier by other authors, have been used to develop a crossover equation of state CR EOS) for square-well fluids with varying well width. The CR EOS for SWF yields the exact second and third virial coefficients, and accurately reproduces first order (high-temperature) perturbation theory results. In addition, the crossover equation of state contains a Ginzburg number, *Gi*, as a parameter, and asymptotically close to the critical point at $|\tau| \ll Gi$ yields the correct scaling exponents for the coexistence curve $\Delta\rho \propto |\tau|^{\beta}$, isothermal susceptibly $\chi_T \propto |\tau|^{-\gamma}$, and isochoric heat capacity $C_V \propto |\tau|^{-\alpha}$. We fit the parameters of our equation of state to one-phase and two-phase thermodynamic data from our simulations and those of previous researchers. The resulting equation of state is found to represent the thermodynamic properties of these square-well fluids to less than 1% deviation in internal energy and density and 0.1% deviation in vapor pressure.